NASA TECHNICAL TRANSLATION NASA TM-76786

METHOD OF PREVENTING OXIDATION OF GRAPHITE FIREPROOF MATERIAL

S. YAMAUCHI, H. SUZUKI

(NASA-TM-76786) METHOD OF PREVENTING OXIDATION OF GRAPHITE FIREPROOF MATERIAL (National Aeronautics and Space Administration) 10 p HC A02/MF A01 CSCI 11D G3/24

N82-16180

Unclas 07984

Translation of Japanese Patent Disclosure Number 29-3485 (1954)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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STANDARD TITLE PAGE

1. Report No. NASA TM-76786	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle METHOD OF PREVENTING OXIDATION OF GRAPHITE FIREPROOF MATERIAL		5. Report Date December 1981 6. Performing Organization Code
7. Author(s) S. Yamauchi and H. Suzuki		8. Performing Organization Report No. 10. Work Unit No.
9. Performing Organization Name and Address Leo Kanner Associates Redwood City, California 94063		11. Contract or Grant No. NASW-3541 13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

Translation of Japanese Patent Disclosure Number 29-3485 (1954).

16. Abstract

A method of preventing oxidation of graphite fireproof material is given, characterized by fine pulverization of a blend of 1 to 33 weight parts alumina and 3 to 19 parts of K_2O + Na_2O in 100 parts of SiO_2, followed by addition of 5 to 160 parts of silicon carbide powder in 100 parts of the mixture. This is thoroughly blended and coated on the surface of graphite fireproof material.

17. Key Words (Selected by Author(s))	18. Distribution Statement		
	Unclassified - Unlimited		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages	22.

NASA-HQ

THE PATENT AGENCY OF JAPAN

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PUBLIC DISCLOSURE OF A PATENT NOTICE

Disclosure Number	29-3485 (1954)
Int. Cl.[2]	20 B 262 (20 B 5)
Date of Disclosure	June 15, 1954
	(total 3 pages)
Application Number	25-10324
Date of Application	August 9, 1950
Applicant, Inventor	S. Yamauchi Tokyo-to, Meguro-ku, Rokugaoka 2340 H. Suzuki Tokyo-to, Ota-ku, Kitasensoku-cho 603

* Numbers in the margin indicate pagination in the Japanese text.

Method of Preventing Oxidation of Graphite Fireproof Material

Detailed Description of the Invention

Graphite fireproof material has many superior properties, but its major defect is that it readily undergoes oxidation at high temperatures. Consequently, graphite fireproof material is the cause of various disturbances since it is incapable of flame calcination and its life is drastically shortened in use.

This invention pertains to a mixture of 100 weight parts of silicic aid (SiO_2), 1 t o 33 parts of alumina (Al_2O_3) and 3 to 19 parts of alkalil metal oxide (K_2O + Na_2O) which is finely pulverized, followed by the addition of 5 to 160 parts of silicon carbide powder. This is then coated on the surface of graphite fireproof material and heated, readily forming a film which prevents oxidation.

Specifically, silicon carbide would be ideal as a constituent element of a film to prevent oxidation of graphite fireproof material since it has intense corrosion resistance even in relation to ash of fuel because of its great thermal conductivity rate and radiant density. However, it must be used in an appropriate blend since it alone does not adhere tightly to the surface of graphite fireproof material. Such a mixture must form a dense film at low temperatures below 900°C at which oxidation of graphite readily occurs, and it must stably maintain silicon carbide even to high temperatures above 1400°C without becoming fluid or bubbling.

Thus, the objective of this invention is to produce a mixture with such properties.

The inventors have considered types of alkali (R_2O) (K_2O and Na_2O separately) and have conducted detailed studies of the reactivity of SiO_2-Al_2O_3-R_2O systems with silicon carbide at high temperatures. They discovered a mixture with the properties suitable for the aforementioned objectives in that system.

Specifically, many experiments revealed that silicon carbide usually decomposes when the temperature exceeds 1250°C when more than 20 parts of P_2O are blended in 100 parts of SiO_2, while a sufficiently air-tight film cannot be produced below 1400°C if the R_2O content is below two parts.

Consequently, the effects resulting from changes in Al_2O_3 were examined in a range of 3 to 19 parts of R_2O in 100 parts of SiO_2. The result was that film did not tightly adhere to fireproof material when the content of Al_2O_3 was below one part, but that abnormal expansion due to free silicic acid resulting primarily from film peeling decreased, and that the adhesion was good (the refractoriness declined somewhat with increase of Al_2O_3 up to a range of 3 to 17 parts, but it posed no practical difficulties). In addition, the silicon carbide did not decompose.

However, the acidity of the mixture gradually decreases with increase in Al_2O_3, and silicon carbide can no longer be stably maintained at high temperatures when the content of Al_2O_3 exceeds 34 parts. The material decomposes, readily producing bubbles.

Thus, it was determined that the blend of SiO_2, Al_2O_3 and R_2O should be in the range of 1 to 30 parts of Al_2O_3 and 3 to 19 parts of R_2O (K_2O + Na_2O) in relation to 100 parts of SiO_2.

Silicon carbide is believed to readily decompose at high temperatures in molten liquid containing alkali. Actually, in experiments producing film by preparing a blend of clay with feldspar, water glass or borax, either alone or blended together, followed by adding silicon carbide to this, molten liquid containing alkalli formed at high temperatures, decomposing the silicon carbide, forming bubbles and destroying the film when the composition was adjusted to prevent oxidation at low temperatures. That indicated that this explanation is correct. However, the results were because the compositions of these mixtures were outside of the aforementioned constituent ranges. In particular,

the results were due to the fact that there were often more than 34 pc s of Al_2O_3 in relation to 100 parts of SiO_2.

A more stable product at high temperatures is produced when there is more K_2O than Na_2O, but a fairly effective film can be formed even if there is a large Na_2O content.

Suitable raw materials which are readily available are used in producing the aforementioned mixture, and the contents may be calculated and blended by the method described below. Fe_2O_3, MgO and CaO are usually present to some extent in these raw materials, but that is permissible so long as their total content is below 7% of total SiO_2 in the mixture. /2

In calculating the blending ranges of the raw materials for producing mixtures, the constituents of the mixture must first be selected within the aforementioned ranges, considering the type and use of fireproof material in which oxidation is to be prevented. Thus, there are various raw materials such as glass or minerals which can be the principal ingredients in SiO_2-alkali-, SiO_2-Al_2O_3- or SiO_2-Al_2O_3-alkali- systems, and they are divided into those with low melting properties and those which are flameproof. Since raw materials with low melting properties generally contain considerable amounts of alkali, virtually all of the permissible amount of alkali in the mixtures is calculated to be supplied in these, and that amount is determined first. Here, natural glass (obsidian, perlite or pitchstone), soda-lime glass fragments, alkaline silicate, feldspar and other available materials are considered to be the raw materials with low melting properties, but there are considerable differences among these in terms of their chemical constituents, melting points, softening points and viscosities of molten liquids. Suitable materials would be used alone or in various blends, depending on the fireproof material whose oxidation is to be prevented, since they have individual chrateristics. Next, the remaining SiO_2 or Al_2O_3 ingredients are alloted to the fireproof raw materials. Since

there are many SiO_2-Al_2O_3 raw materials in the natural world, the most appropriate of them would be selected and used as fireproof raw materials. At this time, chamotte would be used in the raw state as material with great calcination contraction. In addition, adequate caution is required regarding the use of silica since it expands abnormally. The principles in calculation are to allot Al_2O_3 in the SiO_2-Al_2O_3 raw materials, followed by supply of insufficient SiO_2 through silica.

Slight amounts of cordierite or clay may be added in practice to regulate the thermal expansion coefficient and to facilitate application, but these would be treated in proportion to the fireproof raw material, as illustrated in the example.

The fireproof degree of the film increases, but the capability of preventing oxidation declines when an excessive amount of silicon carbide is added to the aforementioned mixture, while the fireproof degree declines, contraction cracks form or the expansion coefficient increases, resulting in peeling when the amount is insufficient. Consequently, a suitable amount in the range of 5 to 160 parts per 100 parts of said mixture would be used depending on the uses and the type of fireproof whose oxidation is to be prevented.

The various raw materials of the mixture are subjected to wet pulverization and thoroughly blended, followed by the addition of silicon carbide powder and water, forming a paste which may be applied to the surface of graphite fireproof material.

A method of implementation of this invention and its effects are described in further detail in the case of a graphite crucible for molten metal as one type of graphite fireproof material.

First, the ingredients of the mixture would form a satisfactory oxidation preventive film if they are in the aforementioned ranges, but since 19.5 parts of Al_2O_3 and 8 parts

of $K_2O + Na_2O$ in 100 parts of SiO_2 was discovered to be an outstanding composition especially in a graphite crucible, they were specified to be the constituent ingredients, and the blending rates of the raw materials were calculated as illustrated below.

	1	2	3			
			SiO_2	Al_2O_3	K_2O+Na_2O	Fe_2O_3 MgO CaO 4
			100.0	19.5	8.6	<7
5	[illegible]	13	8.25	—	8.74	—
6	[illegible]	15	10.78	1.92	0.98	0.21
7	[illegible]	12.3	8.68	0.10	2.15	1.41
8	[illegible]	7.6	4.94	1.52	1.03	0.05
9	[illegible]		33.15	3.03	7.96	1.67
10	[illegible]		66.35	15.47	0.05	<5.33
11	[illegible]	5	2.40	1.70	0.05	0.05
12	[illegible]	5	2.60	1.70	—	0.69

1 name of blended raw material
2 blending amount (weight ratio)
3 specified constituent ingredients of mixture (weight ratio)
4 etc.
5 potassium silicate
6 natural glass (Mikawa cordierite)
7 soda-lime glass fragments
8 Kawabo feldspar
9 total of above raw materials with low melting properties
10 residual amounts of specified composition
11 Motoyama clay
12 cordierite
13 petroleum wax-chamotte
14 Fukushima white silica
15 total of aforementioned side ingredients and fireproof raw materials

/3

Here, the total amount of Fe_2O_3, MgO and CaO is three, which is permissible. Each raw material of the mixture was coarsely ground in advance and weighed out following the calculation results, and all materials were then combined, subjected to wet pulverization using a crucible, and 20 parts of silicon carbide

powder as well as appropriate amounts of water were then added to 100 parts of the mixture which was then thoroughly blended for numerous hours, forming a suitable paste which was applied in an even, thin coating on the surface of a crucible. After drying, this was subjected to calcination at 1250°C. A thin film with good oxidation prevention was formed without any oxidation on the surface of a crucible using a down-draught kiln in calcination without calcination by a reduction flame.

The metal of number 80 and 100 graphite crucibles implemented by this method was melted and the durability was compared with cases in which the preventive method was not implemented. The results are illustrated below.

	durability frequency
material with film based on this method	30-45
material without the film	12-18

However, these results involve dissolution of copper at a surface temperature of the crucible of approximately 1500°C using a fuel oil furnace.

Oxidation of graphite is extreme when the oxidation preventive method is not implemented when a crucible in an oxidative atmosphere such as a fuel oil furnace is used in this fashion. Consequently, the durability frequency is very slight, but when this method is implemented, the durability is 2 to 3.7 times greater since the oxidation action is effectively prevented for prolonged periods of time.

In past implementation of the invention as mentioned above, the material was placed in a conventional reduction flame crucible, coke or graphite powder was plugged in the spaces and calcination was carried out, but high temperature calcination is possible without resorting to such complicated methods and the durability frequency can be markedly increased when the product is used.

Scope of Patent Claim

A method of preventing oxidation of graphite fireproof material characterized by fine pulverization of a blend of 1 to 33 weight parts alumina and 3 to 19 parts of $K_2O + Na_2O$ in 100 parts of SiO_2, followed by the addition of 5 to 160 parts of silicon carbide powder in 100 parts of the mixture. This is thoroughly blended and coated on the surface of graphite fireproof material.